

WHAT IS CLAIMED IS:

1 - A process for the preparation of a fluoroaromatic compound from an aromatic compound carrying at least one amino group on the aromatic ring, characterized in that said aminoaromatic compound is reacted with a nitrosating agent, in the presence of a source of boron trifluoride, in an organic medium, and in that a heat treatment is carried out on the reaction medium comprising the diazonium salt obtained, thus making it possible to directly access the fluoroaromatic compound, by decomposition of the diazonium salt, without intermediate separation of the latter.

15 2 - The process as claimed in claim 1, characterized in that the source of boron trifluoride, the aminoaromatic compound and the organic solvent are introduced in any order; in that the nitrosating agent is introduced; in that the reaction medium is subjected to heat treatment in order to decompose the diazonium salt obtained without it being removed from the medium and in that the fluoroaromatic compound obtained is recovered.

25 3 - The process as claimed in claim 1, characterized in that the diazonium salt formed in the reaction medium is decomposed as it is formed.

4 - The process as claimed in claim 3, characterized in that it comprises the following sequences:

- the source of boron trifluoride, the aromatic compound carrying at least one amino group on the aromatic ring and the organic solvent are mixed by introducing in any order,
- the reaction medium is brought to the decomposition temperature of the diazonium salt,

- the nitrosating agent is gradually added,
- the fluoroaromatic compound formed is recovered.

5 5 - The process as claimed in claim 3, characterized in that it comprises the following sequences:

10 - the source of boron trifluoride, the nitrosating agent and the organic solvent are mixed by introducing in any order,

- the reaction medium is brought to the decomposition temperature of the diazonium salt,

15 - the aromatic compound carrying at least one amino group on the aromatic ring is gradually added,

- the fluoroaromatic compound formed is recovered.

20 6 - The process as claimed in one of claims 1 to 5, characterized in that the source of boron trifluoride is charged at low temperature, the temperature being chosen between -10°C and 20°C, preferably between 0 and 10°C, with the exception of boron trifluoride in the 25 dihydrate form, which is introduced at ambient temperature.

7 - The process as claimed in one of claims 1 to 4, characterized in that the aminoaromatic compound is 30 introduced all at once or gradually.

8 - The process as claimed in one of claims 1 to 7, characterized in that the aminoaromatic compound can be introduced alone or in solution in the organic solvent.

35 9 - The process as claimed in one of claims 1 to 3, 5 to 8, characterized in that the nitrosating agent is introduced all at once or gradually.

10 - The process as claimed in one of claims 1 to 9, characterized in that the nitrosating agent can be introduced alone or in solution in the organic solvent.

5 11 - The process as claimed in one of claims 1 to 10, characterized in that the decomposition temperature of the diazonium salt varies between ambient temperature and 150°C, preferably between 40°C and 130°C.

10 12 - The process as claimed in one of claims 1 to 11, characterized in that the process is carried out at atmospheric pressure but preferably under a controlled atmosphere of inert gases.

15 13 - The process as claimed in one of claims 4, 6 to 12, characterized in that the source of boron trifluoride is charged at low temperature; in that the aminoaromatic compound is gradually added; in that the reaction medium is heated to the decomposition 20 temperature of the diazonium salt and in that the nitrosating agent, preferably an alkyl nitrite, is gradually added.

14 - The process as claimed in claim 13, characterized 25 in that the reaction medium is heated to a temperature of between ambient temperature and 150°C, preferably between 40°C and 130°C.

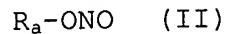
30 15 - The process as claimed in one of claims 1 to 14, characterized in that the fluoroaromatic compound is recovered from the organic phase.

35 16 - The process as claimed in one of claims 1 to 15, characterized in that the nitrosating agent is any proton-free NO<sup>+</sup>-generating source.

17 - The process as claimed in claim 16, characterized in that the nitrosating agent is nitrogen dioxide NO<sub>2</sub>,

nitrogen trioxide  $N_2O_3$ , nitrogen tetroxide  $N_2O_4$  or an alkyl nitrite.

18 - The process as claimed in claim 16, characterized  
5 in that the alkyl nitrite corresponds to the formula  
(II):



in said formula (II),  $R_a$  represents a linear or  
branched alkyl group having from 1 to 12 carbon atoms,  
10 preferably from 1 to 6 carbon atoms, or a cycloalkyl  
group having 5 or 6 carbon atoms.

19 - The process as claimed in claim 18, characterized  
in that the alkyl nitrite is n-butyl, tert-butyl or  
15 isoamyl nitrite.

20 - The process as claimed in one of claims 1 to 19,  
characterized in that the source of boron trifluoride  
is boron trifluoride in the gaseous form or,  
20 preferably, in the complex form.

21 - The process as claimed in claim 19, characterized  
in that the source of fluoride is boron trifluoride in  
combination with a solvent chosen from water, ethers,  
25 alcohols and phenols, acetic acid or acetonitrile.

22 - The process as claimed in claim 19, characterized  
in that the source of fluoride is boron trifluoride in  
combination with a solvent chosen from water, ethyl  
30 ether or acetic acid.

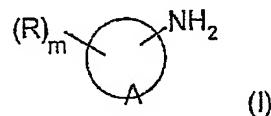
23 - The process as claimed in one of claims 1 to 22,  
characterized in that the reaction is carried out in an  
organic solvent, preferably a polar or nonpolar aprotic  
35 solvent.

24 - The process as claimed in claim 23, characterized  
in that the organic solvent is chosen from: halogenated  
or nonhalogenated aliphatic or aromatic hydrocarbons;

aliphatic, cycloaliphatic or aromatic ethers, or cyclic ethers; aliphatic or aromatic nitriles; linear or cyclic carboxamides; N-methylpyrrolidone.

5 25 - The process as claimed in claim 24, characterized in that the organic solvent is chlorobenzene, 1,2-dichlorobenzene, toluene and benzonitrile.

10 26 - The process as claimed in one of claims 1 to 25, characterized in that the aminoaromatic compound corresponds to the general formula:



in said formula:

15

- A symbolizes the residue of a ring forming all or part of a monocyclic or polycyclic, aromatic, carbocyclic or heterocyclic system,

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- R, which are identical or different, represent substituents on the ring,

- m represents the number of substituents on the ring.

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27 - The process as claimed in claim 26, characterized in that the aminoaromatic compound corresponds to the formula (I) in which A is the optionally substituted residue of a cyclic compound preferably having at least 30 4 atoms in the ring, preferably 5 or 6, and representing at least one of the following rings:

. a monocyclic or polycyclic, aromatic, carbocycle,

35

. a monocyclic or polycyclic, aromatic, heterocycle comprising at least one of the heteroatoms O, N and S.

5 28 - The process as claimed in claim 26, characterized  
in that the optionally substituted residue A represents  
the residue:

1° - of a monocyclic or polycyclic, aromatic, carbocyclic compound,

2° - of a monocyclic or polycyclic, aromatic, heterocyclic compound,

15 3° - of a compound composed of a series of rings, as defined in paragraphs 1 and/or 2, bonded to one another:

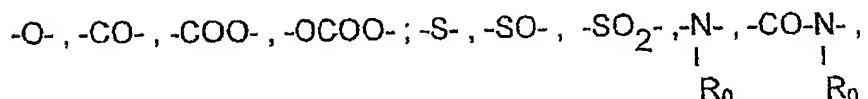
via a valency bond,

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. via an alkylene or alkylidene group having from 1 to 4 carbon atoms, preferably a methylene or isopropylidene group,

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. via one of the following groups:



30 in these formulae,  $R_0$  representing a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms, a cyclohexyl group or a phenyl group.

29 - The process as claimed in claim 26, characterized in that the optionally substituted residue A  
35 represents:

- an aromatic carbocycle,

- an aromatic bicyclic comprising two aromatic carbocycles,

5    - a partially aromatic bicyclic comprising two carbocycles, one of the two of which is aromatic,

- an aromatic heterocycle,

10   - an aromatic bicyclic comprising an aromatic carbocycle and an aromatic heterocycle,

- a partially aromatic bicyclic comprising an aromatic carbocycle and a heterocycle,

15   - an aromatic bicyclic comprising two aromatic heterocycles,

- a partially aromatic bicyclic comprising a carbocycle and an aromatic heterocycle,

20   - a tricycle comprising at least one aromatic carbocycle or heterocycle,

- a series of aromatic carbocycles,

25   - a partially aromatic series of carbocycles,

- a series of an aromatic carbocycle and of an aromatic heterocycle,

30   - a partially aromatic series of a carbocycle and of a heterocycle.

35   30 - The process as claimed in claim 26, characterized in that the optionally substituted residue A represents a benzene, naphthalene, pyridine or quinoline nucleus.

31 - The process as claimed in one of claims 26 to 30, characterized in that the aminoaromatic compound corresponds to the formula (I) in which R, which are identical or different, represent:

5

. a linear or branched alkyl group having from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl or tert-butyl,

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. a linear or branched alkenyl or alkynyl group having from 2 to 6 carbon atoms, preferably from 2 to 4 carbon atoms, such as vinyl or allyl,

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. a linear or branched alkoxy group having from 1 to 6 carbon atoms, preferably from 1 to 4 carbon atoms, such as the methoxy, ethoxy, propoxy, isopropoxy or butoxy groups, an alkenyloxy group, preferably an allyloxy group, or a phenoxy group,

20

. a cyclohexyl, phenyl or benzyl group,

. an acyl group having from 2 to 6 carbon atoms,

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. a group of formula:

-R<sub>1</sub>-OH

-R<sub>1</sub>-SH

-R<sub>1</sub>-COOM

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-R<sub>1</sub>-COOR<sub>2</sub>

-R<sub>1</sub>-CO-R<sub>2</sub>

-R<sub>1</sub>-CHO

-R<sub>1</sub>-N=C=O

-R<sub>1</sub>-N=C=S

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-R<sub>1</sub>-NO<sub>2</sub>

-R<sub>1</sub>-CN

-R<sub>1</sub>-N(R<sub>2</sub>)<sub>2</sub>

-R<sub>1</sub>-CO-N(R<sub>2</sub>)<sub>2</sub>

-R<sub>1</sub>-SO<sub>3</sub>M

-R<sub>1</sub>-SO<sub>2</sub>M

-R<sub>1</sub>-X

-R<sub>1</sub>-CF<sub>3</sub>

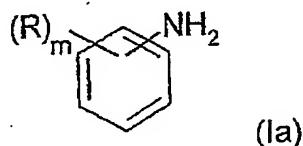
-R<sub>1</sub>-C<sub>p</sub>F<sub>2p+1</sub>

5 in said formulae, R<sub>1</sub> represents a valency bond or a saturated or unsaturated and linear or branched divalent hydrocarbon group, having from 1 to 6 carbon atoms, such as, for example, methylene, ethylene, propylene, isopropylene or isopropylidene; the groups R<sub>2</sub>, which are identical or different, represent a hydrogen atom or a linear or branched alkyl group having from 1 to 6 carbon atoms or a phenyl group; M represents a hydrogen atom, an alkali metal, preferably sodium, 10 or a group R<sub>2</sub>; X symbolizes a halogen atom, preferably a chlorine, bromine, fluorine or iodine atom; p represents a number ranging from 1 to 10.

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32 - The process as claimed in one of claims 26 to 31, 20 characterized in that the aminoaromatic compound corresponds to the formula (I) in which m is a number less than or equal to 4, preferably equal to 1 or 2.

33 - The process as claimed in one of claims 26 to 32, 25 characterized in that the aminoaromatic compound corresponds to the formula (Ia):

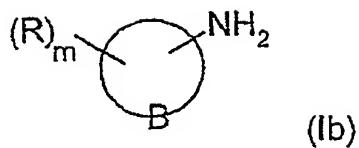


in said formula:

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- R and m have the meaning given above.

34 - The process as claimed in one of claims 26 to 33, characterized in that the aminoaromatic compound 35 corresponds to the formula (Ib):



in said formula:

5 - R and m have the meaning given above,

- B represents the residue of a monocyclic aromatic heterocycle comprising 5 or 6 atoms, one or two of which among them are nitrogen atoms, or the

10 residue of a polycyclic heterocycle comprising, on the one hand, an aromatic heterocycle comprising 5 or 6 atoms, one or two of which among them are nitrogen atoms, and, on the other hand, a carbocycle or a nitrogenous heterocycle which is

15 saturated, unsaturated or aromatic and which comprises 5 or 6 atoms.

35 - The process as claimed in one of claims 26 to 34, characterized in that the aminoaromatic compound is

20 chosen from: 4-bromoaniline, 4-bromo-3-methylaniline, 1-aminonaphthalene, 2-chloro-3-aminopyridine, 3-amino-quinoline or 3-amino-6-methoxyquinoline.